

# REGISTERED COPY PATENT SPECIFICATION

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700.46

Date of filing Complete Specification: Sept. 11, 1951.

Application Date: Oct. 10, 1950. No. 24668/50.

Complete Specification Published: Dec. 2, 1953.

Index at acceptance:—Class 70, E(6G: 19).

## COMPLETE SPECIFICATION

### NOTICE OF AMENDMENT

SPECIFICATION NO. 700,463

The Decision of the Superintending Examiner, acting for the Comptroller-General dated the sixth day of January, 1954, allowed the Application to be amended so as to convert it from one for an independent Patent, into an Application for a Patent of Addition to Patent No. 700,461.

The heading to the Specification has therefore been amended by adding the following clause:— (Patent of Addition to No. 700,461 dated April 23, 1951).

THE PATENT OFFICE,  
3rd February, 1954

DB 41282/1(15)/3365 1FO 2/54

ing it with a per-compound in the presence of a sulphur-containing depolymerisation promoter. In one method of carrying out the invention the rubber is treated in the form of a solution by adding the per-compound and the sulphur-containing depolymerisation promoter to the solution and allowing it to stand until the required degree of depolymerisation has occurred. In a further method of carrying out the invention the rubber is treated while dispersed in an aqueous medium with the per-compound and the sulphur-containing depolymerisation promoter.

It has now been discovered that the depolymerisation of unvulcanised rubber in dispersion or in solution, by means of a per-compound and a sulphur-containing depolymerisation promoter, is due, at least in part, to the presence of free oxygen in the dispersion. If the dispersion containing the per-compound and the sulphur-containing depolymerisation promoter is allowed to stand some diffusion of oxygen from the air into the dispersion occurs which promotes depolymerisation but this is limited to the portions of the

oil mixture of oxygen with one or more other gases, e.g. air, or oxygen-enriched air.

A more extensive depolymerisation can thus be effected in a given time, or alternatively the same degree of depolymerisation can be effected in a smaller time or with the use of a smaller amount of the per-compound. Aeration in accordance with the present invention ensures that oxygen is brought into contact with the whole of the dispersion being treated and the accelerating effect is thus much greater and is more uniform than when the oxygen enters the dispersion adventitiously. Moreover, the rate of depolymerisation is not dependent on the free surface/volume ratio of the dispersion and the depolymerisation treatment of a dispersion can be accelerated considerably even though it has so large a volume that the rate of depolymerisation would not be significantly affected by diffusion of oxygen into it from the air.

The depolymerisation of unvulcanised rubber may be carried out by adding the per-compound and the sulphur-containing depolymerisation promoter to the disper-

[Price 2/8]

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## COMPLETE SPECIFICATION

### Improvements in or relating to the Treatment of Rubber

We, DUNLOP RUBBER COMPANY LIMITED, a British Company, of 1, Albany Street, London, N.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the depolymerisation of unvulcanised rubber and is an improvement in or modification of the invention described and claimed in co-pending Application No. 14056/50 (Serial No. 700,461).

In co-pending Application No. 14056/50 (Serial No. 700,461) there is described an improved method of depolymerising unvulcanised rubber which comprises treating it with a per-compound in the presence of a sulphur-containing depolymerisation promoter. In one method of carrying out the invention the rubber is treated in the form of a solution by adding the per-compound and the sulphur-containing depolymerisation promoter to the solution and allowing it to stand until the required degree of depolymerisation has occurred. In a further method of carrying out the invention the rubber is treated while dispersed in an aqueous medium with the per-compound and the sulphur-containing depolymerisation promoter.

It has now been discovered that the depolymerisation of unvulcanised rubber in dispersion or in solution, by means of a per-compound and a sulphur-containing depolymerisation promoter, is due, at least in part, to the presence of free oxygen in the dispersion. If the dispersion containing the per-compound and the sulphur-containing depolymerisation promoter is allowed to stand some diffusion of oxygen from the air into the dispersion occurs which promotes depolymerisation but this is limited to the portions of the

dispersion adjacent the surface.

It is an object of the invention to provide a method of accelerating the depolymerisation of unvulcanised rubber in the dispersed condition by means of a per-compound and a sulphur-containing depolymerisation promoter.

According to the present invention a method of accelerating the depolymerisation of unvulcanised natural rubber by subjecting a dispersion or solution thereof to the joint action of a per-compound and a sulphur-containing depolymerisation promoter comprises aerating the dispersion or solution of rubber with oxygen or a gas containing free oxygen during the depolymerisation treatment. By a gas containing free oxygen is meant a physical mixture of oxygen with one or more other gases, e.g. air, or oxygen-enriched air.

A more extensive depolymerisation can thus be effected in a given time, or alternatively the same degree of depolymerisation can be effected in a smaller time or with the use of a smaller amount of the per-compound. Aeration in accordance with the present invention ensures that oxygen is brought into contact with the whole of the dispersion being treated and the accelerating effect is thus much greater and is more uniform than when the oxygen enters the dispersion adventitiously. Moreover, the rate of depolymerisation is not dependent on the free surface/volume ratio of the dispersion and the depolymerisation treatment of a dispersion can be accelerated considerably even though it has so large a volume that the rate of depolymerisation would not be significantly affected by diffusion of oxygen into it from the air.

The depolymerisation of unvulcanised rubber may be carried out by adding the per-compound and the sulphur-containing depolymerisation promoter to the disper-

[Price 2/8]

sion of rubber and passing oxygen or air or oxygen-enriched air through the dispersion. Preferably this is done by introducing the gas through a sintered glass plate or other device by which the gas is released into the dispersion in the form of a large number of small bubbles, so that a large gas/dispersion interface is formed. Introduction of the gas may be carried out at ordinary or elevated temperature. A fast stream of gas is not necessary; if sufficient is introduced for a small stream of bubbles to reach the surface, a substantially faster rate will not result if the flow of the gas is increased. The rubber can then be recovered from the dispersion in any appropriate manner, e.g. by coagulation or, in the case of a solution, by evaporating the solvent.

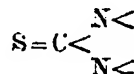
If desired, however, the rubber may be left in the form of a solution or aqueous dispersion for example if it is required for use as an adhesive. The per-compound is gradually decomposed during the depolymerisation treatment and there will in many cases not be sufficient left to cause sufficient further depolymerisation to render the rubber unsuitable for the subsequent use for which it is intended; however, if sufficient per-compound is left to effect the degree of depolymerisation adversely during subsequent storage or use it may be destroyed by treating the dispersion with a reducing agent. The presence of residual sulphur-containing depolymerisation promoter will in general not be disadvantageous, but may in many cases be beneficial during subsequent vulcanisation procedures.

In a preferred form of the invention the depolymerisation is effected while the rubber is in solution, a per-compound and a sulphur-containing depolymerisation promoter being used which are soluble or dispersible in the solution. The rubber may instead be depolymerised while dispersed in an aqueous medium; either as a natural rubber latex or as an artificially prepared aqueous dispersion of natural rubber, in which case a per-compound and a sulphur-containing depolymerisation promoter are selected which are soluble or dispersible in water and which do not cause coagulation of the rubber.

The per-compound may be an organic peroxide or hydroperoxide; it may be an alkyl hydroperoxide for example tertiary-butyl hydroperoxide, or an acyl or aroyl peroxide, for example benzoyl peroxide, and it may be added to the rubber dispersion in an amount of from 0.02% to 15% by weight of the rubber. The sulphur-containing depolymerisation promoter may also be used in amounts of the order of 0.02% to 10% by weight of the

rubber, the amount selected in any particular case being preferably less than the weight of the per-compound.

Compounds which may be used as sulphur-containing depolymerisation promoters are organic compounds having both a nitrogen atom and a sulphur atom directly linked to a carbon atom. The use of compounds of this type as depolymerisation promoters is described and claimed in copending Applications Nos. 13261/50 and 13262/50 (Serial No. 694,317). Suitable compounds include thiocarbonyl compounds whose thiocarbonyl carbon atom is directly linked to two nitrogen atoms; examples are heterocyclic compounds containing the group



where the thiocarbonyl carbon atom forms part of a five- or six- membered ring; e.g. thiouracil; 1-hydrobenzimidazole-2-thione, (also known by the name of its tautomeric form 2-mercaptobenzimidazole); 1,2-dihydroimidazole-2-thione and ethylene thiourea.

In the preferred form of the invention in which the rubber is treated in solution, solid rubber may be given a short mastication treatment beforehand to facilitate the subsequent step of dissolving it in the solvent. This mastication may be effected in the presence of a per-compound and a sulphur-containing depolymerisation promoter as described in copending Application No. 14056/50 (Serial No. 700,461).

The invention is of particular value for producing rubber in a soft putty like or viscous liquid condition. The rubber so obtained may be compounded with vulcanising agents and used as an adhesive or as a filler, or for making article by a casting process.

The following examples illustrate the invention, all parts being by weight.

#### EXAMPLE 1.

Smoked sheet rubber was milled on open rolls at 60° C. for 15 minutes with 0.2% by weight of mercaptobenzimidazole and 0.5% by weight of tertiary butyl hydroperoxide to render it more easily soluble. 300 parts of the milled rubber were dissolved in 1,500 parts of benzene, 6 parts of mercaptobenzimidazole and 6 parts of tertiary butyl hydroperoxide were then added and oxygen was bubbled through the solution for 48 hours, thorough dispersion of the oxygen being achieved by delivering it through a sintered glass inlet. Some benzene was lost during this process by evaporation. At the end of this time the solution was made up to its

original bulk by the addition of benzene and the viscosity of the solution, which gives an indication of the degree of depolymerisation, was determined at 20° C. The solution had a viscosity of 0.24 poises. When a similar quantity of solution prepared from rubber milled in the same way was agitated in a closed vessel containing air with the same quantities of mercaptobenzimidazole and tertiary butyl hydroperoxide for 72 hours, the viscosity of the solution obtained was 39 poises.

#### EXAMPLE 2.

Smoked sheet rubber was masticated on a mill with 0.2% by weight of mercaptobenzimidazole and 0.5% by weight of tertiary butyl hydroperoxide for ten minutes. The rubber was then dissolved in petroleum naphtha to give a 10% wt./vol. solution. This solution had a viscosity at 20° C. of 32.4 poises.

To a litre of this solution was then added 10% by weight of tertiary butyl hydroperoxide and 6% by weight of mercaptobenzimidazole (calculated on the weight of the rubber) and oxygen was bubbled slowly through the solution for six hours. At the end of this time the viscosity of the solution at 20° C. had decreased to 0.30 poises.

A further litre of the solution was allowed to stand in air without agitation for six hours. The viscosity of the solution had then decreased to 4.74 poises.

#### EXAMPLE 3.

Smoked sheet rubber was masticated on a mill with 0.2% by weight of mercaptobenzimidazole and 0.5% by weight of tertiary butyl hydroperoxide for 10 minutes, and from the thus masticated rubber a solution in benzene containing 10% (weight/volume) of rubber was made. The solution had a viscosity at 20° C. of 35.6 poises. To a litre of this solution was added 10% by weight of tertiary butyl hydroperoxide and 6% by weight of mercaptobenzimidazole, each calculated on the weight of the rubber, and oxygen was bubbled through the solution for six hours. The viscosity of the solution at 20° C. was then 0.22 poises.

A further litre of the solution was treated by adding the same amounts of mercaptobenzimidazole and tertiary butyl hydroperoxide as above and passing air through the solution slowly for 6 hours; the viscosity of the solution had decreased to 0.35 poises.

For comparison two further quantities of the solution (each of 1 litre) were mixed with (a) 6% mercaptobenzimidazole and (b) 10% of tertiary butyl hydroperoxide, each calculated on the weight of the rubber, and similarly treated with oxygen for 6 hours. The viscosity at 20°

C. of the solution decreased respectively to (a) 34.6 poises and (b) 16.6 poises.

#### EXAMPLE 4.

Smoked sheet rubber was masticated on a mill as described in example 3, and from the thus masticated rubber a solution in benzene was made containing 15% (weight/volume) of rubber. The solution had a viscosity of 150 poises at 20° C. To a litre of this solution was added 10% by weight of tertiary butyl hydroperoxide and 6% by weight of mercaptobenzimidazole (calculated on the weight of the rubber); and oxygen was bubbled through the solution for six hours. The viscosity of the solution at 20° C. had then decreased to 0.58 poises.

A further part of the solution was treated by adding the same amount of mercaptobenzimidazole and tertiary butyl hydroperoxide as above and passing air through the solution for 6 hours. The viscosity of the solution at 20° had then decreased to 0.47 poises.

For comparative purposes two further parts of the solution were mixed with (a) 6% of mercaptobenzimidazole and (b) 10% by weight of tertiary butyl hydroperoxide, each calculated on the weight of the rubber, and oxygen was passed through each solution as above for 6 hours. The viscosity of the two solutions at 20° C. had then decreased respectively to (a) 140 poises and (b) 36.2 poises.

In each of the above examples the introduction of air or oxygen was regulated so that a slow stream of bubbles reached the surface of the solution. When the treatment with air or oxygen according to the invention was complete substantially all the per-compound had been decomposed. The rubber was recovered by evaporation of the solvent. The rubber obtained in those examples in which oxygen was used for the treatment (Examples 1, 2 and 4) was a viscous liquid, and the rubber obtained in which air was used for the treatment (Example 3) was a soft slightly elastic putty-like material.

What we claim is:—

1. A method of accelerating the depolymerisation of unvulcanised natural rubber by subjecting a dispersion or solution thereof to the joint action of a per-compound and a sulphur-containing depolymerisation promoter which comprises aerating the dispersion or solution with oxygen or a gas containing free oxygen during the depolymerisation treatment.

2. A method according to claim 1 in which the rubber is depolymerised while dissolved in a volatile solvent therefor.

3. A method according to claim 1 or claim 2 in which the per-compound is present in an amount between 0.02% and

15% by weight of the rubber and the sulphur-containing depolymerisation promoter is present in amount between 0.02% and 10% by weight of the rubber.

5 4. A method according to any of the preceding claims in which the sulphur-containing depolymerisation promoter is a compound having both a nitrogen atom and a sulphur atom directly linked to a carbon atom.

10 5. A method according to claim 4 in which the sulphur-containing depolymerisation promoter is a heterocyclic compound containing the group



where the thiocarbonyl carbon atom forms part of a five- or six-membered ring.

6. A method according to claim 5 in which the sulphur-containing depoly-

merisation promoter is mercaptobenzimidazole. 20

7. A method according to any of the preceding claims in which the per-compound is an alkyl hydroperoxide.

8. A method of accelerating the depolymerisation of unvulcanised natural rubber by subjecting a dispersion thereof to the joint action of a per-compound and a sulphur-containing depolymerisation promoter in which the dispersion is aerated with oxygen or a physical mixture of oxygen with one or more other gases, substantially as hereinbefore described with reference to the foregoing examples. 25 30 35

9. Depolymerised unvulcanised natural rubber and dispersions or solutions thereof whenever obtained by a process according to any of the preceding claims.

G. W. I. SHEAVYN,  
Agent for the Applicants.

## PROVISIONAL SPECIFICATION

### Improvements in or relating to the Treatment of Rubber

40 We, DUNLOP RUBBER COMPANY LIMITED, a British Company of 1, Albany Street, London, N.W.1, do hereby declare this invention to be described in the following statement:—

45 This invention relates to improvements in depolymerising unvulcanised rubber.

In co-pending Application No. 14056/50 (Serial No. 700,461) there is described an improved method of depolymerising unvulcanised rubber which comprises treating it with a per-compound in the presence of a sulphur-containing depolymerisation promoter. In one method of carrying out the invention the rubber is treated in the form of a solution by adding the per-compound and the sulphur-containing depolymerisation promoter to the solution and allowing it to stand until the required degree of depolymerisation has occurred. In a further method of carrying out the invention the rubber is treated while dispersed in an aqueous medium with the per-compound and the sulphur-containing depolymerisation promoter. 50 55 60 65

It has now been found that in depolymerising rubber in a dispersed condition by means of a per-compound and sulphur-containing depolymerisation promoter, it is advantageous to subject the dispersion to the action of oxygen or an oxygen-containing gas during the depolymerisation treatment. A more extensive depolymerisation can thus be effected in

a given time, or alternatively the same degree of depolymerisation can be effected in a smaller time or with the use of a smaller amount of the per-compound. 75

The rubber may be dispersed in a solvent therefor, i.e. be in the form of a solution, or it may be dispersed in a non-solvent liquid, e.g. as a natural latex or as an artificially prepared dispersion in an aqueous medium. 80

In one method of carrying out the invention depolymerisation is effected by adding the per-compound and the sulphur-containing depolymerisation promoter to a solution of rubber and bubbling oxygen through the solution at ordinary or elevated temperature until the desired degree of depolymerisation has been effected. 85 90

Preferably the per-compound is an organic peroxide or a hydroperoxide, for example tertiary butyl hydroperoxide or an acyl or aroyl peroxide, for example benzoyl peroxide. The depolymerisation promoter may be an organic compound soluble in the rubber solution and containing both a nitrogen atom and a sulphur atom directly linked to a carbon atom. Suitable depolymerisation promoters which may be used are further described in the above-mentioned co-pending Application No. 14056/50 (Serial No. 700,461). 95 100 105

The following Example illustrates the invention, all parts being by weight.

**EXAMPLE.**

100 parts of smoked sheet rubber were milled on open rolls at 60° C. for 15 minutes with 0.2 parts of mercaptobenzimidazole and 0.5% of tertiary butyl hydroperoxide to render it more easily soluble. 300 parts of the milled rubber were dissolved in 1,500 parts of benzene. 6 parts of mercaptobenzimidazole and 6 parts of tertiary butyl hydroperoxide were then added and oxygen was bubbled through the solution for 48 hours, thorough dispersion of the oxygen being achieved by delivering it through a sintered glass inlet. At the end of this time the solution was made up to its original

bulk by the addition of benzene and the viscosity of the solution, which gives an indication of the degree of depolymerisation, was determined at 20° C. The solution had a viscosity of 0.24 poises.

When a similar quantity of solution prepared from rubber milled in the same way was agitated in a closed vessel containing air with the same quantities of mercaptobenzimidazole and tertiary butyl hydroperoxide for 72 hours, the viscosity of the solution obtained was 39 poises.

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Agent for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1953.  
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.